

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 08-295723

(43)Date of publication of application : 12.11.1996

(51)Int.Cl.

C08G 59/50
C08G 73/00
C08J 5/24
C08J 5/24
C08L 63/00
C08L 79/08
C09J179/08

(21)Application number : 07-103443

(71)Applicant : HITACHI CHEM CO LTD

(22)Date of filing : 27.04.1995

(72)Inventor : IJIMA TOSHIYUKI

NAKAMURA YOSHIHIRO

MURAI AKIRA

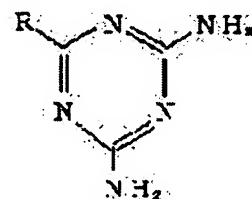
SAKAI HIROSHI

(54) THERMOSETTING POLYIMIDE RESIN COMPOSITION AND PRODUCTION OF
THERMOSETTING POLYIMIDE RESIN PREPREG

(57)Abstract:

PURPOSE: To provide a resin composition which can give a non-flow prepreg without using any modified resin by adding 2,4-diamino-s-triazine to a mixture comprising a thermosetting polyimide resin and an epoxy resin.

CONSTITUTION: 2,4-Diamino-s-triazine is added to a mixture comprising a thermosetting polyimide resin and an epoxy resin to obtain a thermosetting polyimide resin composition. This composition is dissolved in an organic solvent to form a varnish, a fibrous base is impregnated with the varnish, and the resin is cured by heating to stage B to obtain a prepreg. Although a resin composition of this kind (e.g. a resin composition formed by mixing a thermosetting polyimide resin with an epoxy resin, dicyandiamide and a modified resin) has controlled resin flow, it has drawbacks that the heat resistance is lowered, and the modified resin is eluted or swollen by chemical treatment. this composition can give a uniform prrepreg having low flow without using any modified resin.



AN 1997:79918 CAPLUS
 DN 126:105182
 ED Entered STN: 03 Feb 1997
 TI Manufacture of thermosetting polyimide compositions and their prepregs with low fluidity
 IN Iijima, Toshuki; Nakamura, Yoshihiro; Murai, Akira; Sakai, Hiroshi
 PA Hitachi Chemical Co Ltd, Japan
 SO Jpn. Kokai Tokkyo Koho, 4 pp.
 CODEN: JKXXAF
 DT Patent
 LA Japanese
 IC ICM C08G059-50
 ICS C08G073-00; C08J005-24; C08L063-00; C08L079-08; C09J179-08
 CC 38-3 (Plastics Fabrication and Uses)
 Section cross-reference(s): 37, 76

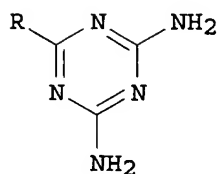
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 08295723	A2	19961112	JP 1995-103443	19950427
	JP 3653784	B2	20050602		
	JP 2004247761	A2	20040902	JP 2004-146853	20040517
PRAI	JP 1995-103443	A3	19950427		

CLASS

PATENT NO.	CLASS	PATENT FAMILY CLASSIFICATION CODES
JP 08295723	ICM	C08G059-50
	ICS	C08G073-00; C08J005-24; C08L063-00; C08L079-08; C09J179-08
JP 2004247761	FTERM	4F072/AA04; 4F072/AA07; 4F072/AB09; 4F072/AB28; 4F072/AD27; 4F072/AD45; 4F072/AE01; 4F072/AF28; 4F072/AG03; 4F072/AH02; 4F072/AK14; 4F072/AL13; 4J002/CD00X; 4J002/CD05X; 4J002/CD06X; 4J002/CM04W; 4J002/EU186; 4J002/FD146; 4J002/GQ00; 5E346/AA12; 5E346/BB01; 5E346/CC02; 5E346/CC09; 5E346/CC10; 5E346/DD02; 5E346/EE02; 5E346/EE06; 5E346/EE07; 5E346/EE09; 5E346/EE44; 5E346/GG02; 5E346/GG28; 5E346/HH33

GI



I

AB The prepregs, useful for adhesion of printed circuit boards, are manufactured by dissolving compns. comprising thermosetting polyimides, epoxy resins, and 2,4-diamino-s-triazine derivs. I (R = C1-11 alkyl, Ph) in solvents, impregnating into fiber materials, and curing by heating. Thus Kelimide 601 25, Epikote 154 25, and acetoguanamine 5 parts were dissolved in dimethylacetoamide, impregnated into glass cloth, and cured at 160° for 20 min to give a prepreg showing low fluidity, glass temperature 176°, and no voids.

ST epoxy polyimide prepreg diaminotriazine deriv hardener; fluidity epoxy resin polyimide prepreg adhesive; printed circuit board epoxy polyimide prepreg

IT Polyimides, uses
 Polyimides, uses
 RL: IMF (Industrial manufacture); PRP (Properties); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)

(epoxy; manufacture of preregs containing thermosetting polyimides, epoxy resins, and diaminotriazine hardeners with low flexibility for adhesion of printed circuit boards)

IT Adhesives

Crosslinking agents

Printed circuit boards

(manufacture of preregs containing thermosetting polyimides, epoxy resins, and diaminotriazine hardeners with low flexibility for adhesion of printed circuit boards)

IT Glass fiber fabrics

RL: MOA (Modifier or additive use); TEM (Technical or engineered material use); USES (Uses)

(manufacture of preregs containing thermosetting polyimides, epoxy resins, and diaminotriazine hardeners with low flexibility for adhesion of printed circuit boards)

IT Epoxy resins, uses

Epoxy resins, uses

RL: IMF (Industrial manufacture); PRP (Properties); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)

(polyimide-; manufacture of preregs containing thermosetting polyimides, epoxy resins, and diaminotriazine hardeners with low flexibility for adhesion of printed circuit boards)

IT 542-02-9, Acetoguanamine

RL: MOA (Modifier or additive use); PRP (Properties); TEM (Technical or engineered material use); USES (Uses)

(crosslinking agents, for epoxy polyimides; manufacture of preregs containing

thermosetting polyimides, epoxy resins, and

diaminotriazine hardeners with low flexibility for adhesion of printed circuit boards)

IT 185623-73-8P

RL: IMF (Industrial manufacture); PRP (Properties); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)

(manufacture of preregs containing thermosetting polyimides, epoxy resins, and diaminotriazine hardeners with low flexibility for adhesion of printed circuit boards)

RN 542-02-9 REGISTRY

ED Entered STN: 16 Nov 1984

CN 1,3,5-Triazine-2,4-diamine, 6-methyl- (9CI) (CA INDEX NAME)

OTHER CA INDEX NAMES:

CN s-Triazine, 2,4-diamino-6-methyl- (6CI, 8CI)

OTHER NAMES:

CN 2,4-Diamino-6-methyl-1,3,5-triazine

CN 2,4-Diamino-6-methyl-s-triazine

CN 2,6-Diamino-4-methyl-s-triazine

CN 2-Methyl-4,6-diamino-s-triazine

CN 6-Methyl-1,3,5-triazine-2,4-diamine

CN Acetoguanamine

CN ENT 50715

CN NSC 257

FS 3D CONCORD

MF C4 H7 N5

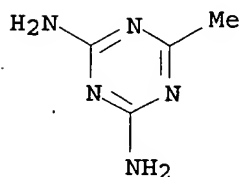
CI COM

LC STN Files: BEILSTEIN*, CA, CAOLD, CAPLUS, CASREACT, CHEMCATS,
CHEMINFORMRX, CHEMLIST, CSCHEM, IFICDB, IFIPAT, IFIUDB, PROMT, SPECINFO,
TOXCENTER, USPAT2, USPATFULL

(*File contains numerically searchable property data)

Other Sources: DSL**, EINECS**, TSCA**

(**Enter CHEMLIST File for up-to-date regulatory information)



PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

310 REFERENCES IN FILE CA (1907 TO DATE)

51 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA

311 REFERENCES IN FILE CAPLUS (1907 TO DATE)

22 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

DERWENT-ACC-NO: 1997-038036

DERWENT-WEEK: 200537

COPYRIGHT 2005 DERWENT INFORMATION LTD

TITLE: Thermosetting polyimide resin compsn. used for adhesion
of composite PWB- comprises thermosetting polyimide
resin, epoxy resin and 2,4- di:amino - S - triazine

PATENT-ASSIGNEE: HITACHI CHEM CO LTD[HITB]

PRIORITY-DATA: 1995JP-0103443 (April 27, 1995)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAINIPC
JP 3653784 B2	June 2, 2005	N/A	006	C08L 063/00
<u>JP 08295723 A</u>	November 12, 1996	N/A	004	C08G 059/50

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
JP 3653784B2	N/A	1995JP0103443	April 27, 1995
JP 3653784B2	Previous Publ.	JP 8295723	N/A
JP 08295723A	N/A	1995JP0103443	April 27, 1995

INT-CL (IPC): C08G059/50, C08G073/00, C08J005/24, C08L063/00,
C08L079/08, C09J179/08, H05K001/02, H05K003/28, H05K003/46

RELATED-ACC-NO: 2004-638323

ABSTRACTED-PUB-NO: JP 08295723A

BASIC-ABSTRACT:

A thermosetting polyimide resin compsn. comprises a thermosetting polyimide resin, an epoxy resin, and a 2,4diamino-s-triazine of formula (1):

R = 1 - 11 C alkyl gp. or phenyl gp.

Also claimed is a process for preparing a thermosetting polyimide resin prepreg comprising impregnation of a varnish, in which the thermosetting polyimide resin compsn. has been dissolved in an organic solvent, into a textile substrate, and then heat curing the resin to B stage.

USE - Prepn. of a thermosetting polyimide resin prepreg which is used for adhesion between a printed wiring board of a composite type consisting of a rigid printed wiring board and a flexible printed wiring board.

ADVANTAGE - This resin compsn. gives a prepreg., which has no flow and flow homogeneity, without adding a modified resin.

CHOSEN-DRAWING: Dwg.0/0

TITLE-TERMS: THERMOSETTING POLYIMIDE RESIN COMPOSITION ADHESIVE COMPOSITE PWB
COMPRISE THERMOSETTING POLYIMIDE RESIN POLYEPOXIDE RESIN DI AMINO
TRIAZINE

ADDL-INDEXING-TERMS:

PRINTED WIRING BOARD

DERWENT-CLASS: A26 A85 G03 L03 V04 X12

CPI-CODES: A05-A01B; A05-J01A; A08-D03; A08-R01; A12-E07A; G03-B02E;
G03-B02E2; L03-H04E9;

* NOTICES *

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the manufacture approach of a thermosetting polyimide resin constituent and thermosetting polyimide resin prepreg.

[0002]

[Description of the Prior Art] The prepreg called no flow prepreg is used for adhesion of the printed wired board which carried out the combination unification of a rigid printed wired board and the flexible printed wiring board. Unlike the prepreg for pasting up between inner layer circuit plates and a inner layer circuit plate, and outer layer material, this no flow prepreg is prepreg with very few (10% or less) resin streaks, when manufacturing the usual multilayer printed wiring board. A resin streak is lessened for making it the resin of prepreg not overflow into the field of a flexible printed wiring board, when carrying out the combination unification of a rigid printed wired board and the flexible printed wiring board.

[0003] Thus, as a resin presentation of the prepreg for adhesion with few resin streaks, thermosetting polyimide resin, an epoxy resin, and a dicyandiamide (it acts as a curing agent of an epoxy resin) are used as a fundamental component, and what blended the hardening accelerator, for example, an imidazole, as occasion demands is used. If heating time when manufacturing prepreg is generally lengthened or whenever [stoving temperature] is made high, a resin streak will decrease. However, in the resin presentation which uses thermosetting polyimide resin, an epoxy resin, and a dicyandiamide as a fundamental component, a resin streak cannot obtain uniform prepreg by this approach. Then, he adds modified resin to the resin presentation of the prepreg for adhesion, and is trying to adjust a resin streak. As modified resin, the resin which has epoxy acrylate and a rubber elasticity property is used.

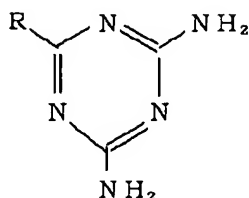
[0004]

[Problem(s) to be Solved by the Invention] However, if modified resin is added, Tg of the resin after hardening will become low and the thermal resistance of a printed wired board will worsen. Moreover, since thermal expansion becomes large, through hole dependability is spoiled. Furthermore, there was a fault of the added modified resin having been eluted by the chemical treatment after multilayering, or swelling. This invention tends to obtain the resin constituent which can obtain no flow prepreg without adding modified resin.

[0005]

[Means for Solving the Problem] this invention persons repeated examination variously about conditions for a resin streak to obtain few and uniform prepreg, and when the mixture of thermosetting polyimide resin and an epoxy resin was stiffened by 2 expressed with ** 2, and 4-diamino-s-triazine, they found out that it was easy to control a resin streak to homogeneity.

[Formula 2]



Rは、炭素数1～11のアルキル基又はフェニル基である。

[0006] What is necessary is for there to be no limit and to just be used for the printed circuit board generally about thermosetting polyimide resin and especially an epoxy resin. As 2 and 4-diamino-s-triazine, acetoguanamine, vinyl triazine, benzoguanamine, etc. are mentioned as 2 and 4-diamino-s-triazine. Moreover, the KERUIMIDO 601 grade of the heat-curing mold addition mold maleimide system polyimide resin S.A., for example, Rhone Poulenc, with which thermosetting polyimide resin is marketed is used. Furthermore, especially if epoxy resins are two or more organic functions, there will be no limit and the bisphenol A jig RIJIRU ether, the diglycidyl ether of FE Norian novolak resin, etc. will be used. These loadings are thermosetting polyimide resin 10 - 80 weight sections, epoxy resin 20 - 90 weight sections, 2, and 4-diamino-s-triazine 1 - 20 weight sections. When 3-10 weight section combination of the 2 and 4-diamino-s-triazine is carried out especially, control of a resin streak is easy.

[0007] Although the thermosetting polyimide resin constituent of this invention dissolves in an organic solvent, and is used as a varnish, and this is sunk in and heated to a fiber base material, and resin is stiffened to B stage and considered as prepreg, the conditions at this time adjust a resin streak. That is, if hardening of resin is advanced, a resin streak will decrease.

[0008] It depends on the reactivity of the resin in coating temperature for control of the resin streak when considering as prepreg. The reactivity of prepreg resin combination can be measured with a differential scanning calorimeter (it describes below as Differential Scanning Calorimeter DSC). In order to obtain the stable resin streak, 130-150 degrees C and exothermic peak temperature have to make it become 220-250 degrees C the good exoergic initiation temperature measured by DSC. Conventionally, fatty amine fatty amines, such as a dicyandiamide currently used abundantly as a curing agent of the prepreg for multilayering, have a 130-160 degrees C [which is coating temperature] active reaction, the exoergic initiation temperature measured by DSC is 110 degrees C, and exothermic peak temperature is 200 degrees C.

[0009]

[Example] The thermosetting polyimide resin (KERUIMIDO 601 by French Rhone Poulenc S.A.) 25 weight section, the phenol novolak mold epoxy resin (Epicoat 154 by oil-ized shell incorporated company) 25 weight section, and the acetoguanamine 5 weight section were dissolved in the dimethylacetamide 45 weight section, and the epoxy denaturation polyimide resin combination varnish was prepared. In addition, when the reactivity of this resin combination was measured by DSC by programming-rate: 10 degrees C /, and min (room temperature -> 300 degrees C), exoergic initiation temperature was 146 degrees C, and exothermic peak temperature was 236 degrees C.

[0010] To glass fabrics with a thickness of 0.1mm, the amount of hard resin sank in, it heated said epoxy denaturation polyimide resin combination varnish for 20 minutes at 160 degrees C, and obtained prepreg to them so that it might become 52 % of the weight.

[0011] The example of comparison 1 thermosetting polyimide resin (KERUIMIDO 601 by French Rhone Poulenc S.A.) 25 weight section, the phenol novolak mold epoxy resin (Epicoat 154 by oil-ized shell incorporated company) 25 weight section, and the dicyandiamide 5 weight section were dissolved in the dimethylacetamide 45 weight section, and the epoxy denaturation polyimide resin combination varnish was prepared. In addition, the exoergic initiation temperature of this resin presentation was 116 degrees C, and exothermic peak temperature was 204 degrees C. Prepreg was obtained like said example below.

[0012] The example of comparison 2 thermosetting polyimide resin (KERUIMIDO 601 by French Rhone Poulenc S.A.) 25 weight section, the phenol novolak mold epoxy resin (Epicoat 154 by oil-ized shell incorporated company) 25 weight section, the dicyandiamide 5 weight section, and the epoxy

acrylate 20 weight section were dissolved in the dimethylacetamide 45 weight section, and the epoxy denaturation polyimide resin combination varnish was prepared. In addition, the exoergic initiation temperature of this resin presentation was 116 degrees C, and exothermic peak temperature was 204 degrees C.

[0013] The resin streak was investigated about the prepreg obtained above. Moreover, it heated for 90 minutes at 170 degrees C, resin was stiffened, and Tg was investigated. Next, the prepreg obtained between the rigid printed boards and the flexible printed wiring boards in which the circuit was formed was inserted, heating application of pressure was carried out by the temperature of 170 degrees C, and pressure 2.5MPa, and the rigid printed board and the flexible printed wiring board were unified. And the existence and through hole dependability of void generating were investigated. The result was as in a table 1.

[0014] The measuring method of a resin streak is as follows (IPC-TM-65 conformity). From the place which went into 25mm or more inside from the edge of prepreg, the four-sheet bias cut of the sample of 101.6mm angle is carried out, and weight (initial mass) is measured. From the roll of prepreg, a sample is extracted at the predetermined spacing and prepared several sets. A direction is arranged, the sample of four sheets is piled up, it inserts with a steel plate through the film of the Pori vinyl fluoride, and heating application of pressure is carried out for 10 minutes by 171 degrees C and 1.37MPa. It pierces in a disc with a diameter of 81.1mm from the center of the sample after cooling, the weight of the pierced disc is measured, and a resin streak is calculated by the following formula (several 1).

[Equation 1] Resin streak (%) = $100 \times (\text{initial-mass} - 2 \times \text{disc weight}) / \text{initial mass}$ [0015] The existence of a void was investigated as follows. A clearance hole with a diameter of 1.6mm is prepared all over the front flesh side of double-sided copper clad laminate (35 micrometers in copper foil thickness) with a base material thickness of 0.1mm, and the circuit pattern which made the rate of residual copper 50% is created. The copper foil with a thickness of 18 micrometers is piled up through the prepreg tested to the both sides, and heating application of pressure is carried out for 90 minutes by 170 degrees C and 2.5MPa. And etching clearance of the copper foil of an outer layer is carried out, and the embedding to a clearance hole is investigated.

[0016] Through hole dependability was investigated as follows. The copper foil with a thickness of 18 micrometers is put on a ten-sheet pile and its outside, and heating application of pressure of the prepreg to test is carried out for 90 minutes by 170 degrees C and 2.5MPa. A through hole with a diameter of 0.4mm is prepared, and through-hole plating is carried out so that the plating thickness in a hole may be set to 35 micrometers. It is processed into a circuit pattern which flows through a front flesh-side circuit by turns between through hole 100 holes after that. and a 20**2-degree C stream -- let [a tub] immersion be 1 cycle for 10 seconds for 10 seconds at immersion, 260**2-degree C HOTSU, and an oil tub -- hot oil trial 100 cycle operation is carried out.

[0017]

[A table 1]

	実施例	比較例 1	比較例 2
樹脂流れ (%)	3.5	10.7	8.6
樹脂流れのばらつき (%)	2.1~5.5	0.1~15.2	2.0~9.0
Tg (℃)	176	167	57
ボイドの有無	○	△~×	○
スルーホール信頼性	異常無し	断線	断線

existence [of a void]: -- abnormality [in O;] nothing, and **; -- those small with a void, x; void frequent occurrence, or an open circuit [0018] the resin constituent of a table 1 to an example -- as prepreg -- the time -- a resin streak -- control is easy and a top with little resin streak dispersion of a

throughout [it is carrying out coating on the same conditions] understands that Tg after hardening is high. Moreover, generating of the void after adhesion is also accepted and **** and through hole dependability are also good.

[0019]

[Effect of the Invention] As a curing agent of an epoxy denaturation polyimide resin constituent, by using 2 and 4-diamino-s-triazine, although modified resin is blended and it drops off, according to this invention, the resin streak of prepreg is made to homogeneity few.

[Translation done.]

* NOTICES *

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

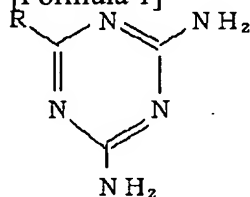
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] 2 expressed with thermosetting polyimide resin, an epoxy resin, and ** 1, the thermosetting polyimide resin constituent which consists of 4-diamino-s-triazine.

[Formula 1]



Rは、炭素数1～11のアルキル基又はフェニル基である。

[Claim 2] The manufacture approach of the thermosetting polyimide resin prepreg characterized by sinking in and heating the varnish which dissolved the thermosetting polyimide resin constituent of claim 1 in the organic solvent to a fiber base material, and stiffening resin to B stage.

[Translation done.]

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平8-295723

(43) 公開日 平成8年(1996)11月12日

(51)Int.Cl. ⁸	識別記号	庁内整理番号	P I		技術表示箇所
C 0 8 G 59/50	N J E		C 0 8 G 59/50	N J E	
73/00	N T B		73/00	N T B	
C 0 8 J 5/24			C 0 8 J 5/24		
	C F G			C F G	
C 0 8 L 63/00	N K A		C 0 8 L 63/00	N K A	
審査請求 未請求 請求項の数 2 O L (全 4 頁) 最終頁に続く					

(21)出願番号	特願平7-103443	(71)出願人	000004455 日立化成工業株式会社 東京都新宿区西新宿2丁目1番1号
(22)出願日	平成7年(1995)4月27日	(72)発明者	飯島 利行 茨城県下館市大字小川1500番地 日立化成 工業株式会社下館工場内
		(72)発明者	中村 吉宏 茨城県下館市大字小川1500番地 日立化成 工業株式会社下館工場内
		(72)発明者	村井 曜 茨城県下館市大字小川1500番地 日立化成 工業株式会社下館工場内
		(74)代理人	弁理士 廣瀬 章

最終頁に続く

(54) 【発明の名称】 熱硬化性ポリイミド樹脂組成物及び熱硬化性ポリイミド樹脂プリプレグの製造方法

(57) 【要約】

【目的】 樹脂流れが小さく、かつ均一なエポキシ変性ポリイミド樹脂プリプレグ。

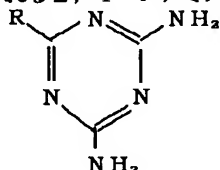
【構成】 熱硬化性ポリイミド樹脂、エポキシ樹脂及び2, 4-ジアミノ-s-トリアジンからなる熱硬化性ポリイミド樹脂組成物ワニスを繊維基材に含浸し、加熱して樹脂をBステージ迄硬化させる。

1

2

【特許請求の範囲】

【請求項1】 熱硬化性ポリイミド樹脂、エポキシ樹脂及び化1で表される2, 4-ジアミノ-s-トリアジン*



Rは、炭素数1～11のアルキル基又はフェニル基である。

【請求項2】 請求項1の熱硬化性ポリイミド樹脂組成物を有機溶剤に溶解したワニスを繊維基材に含浸し、加熱して樹脂をBステージに硬化させることを特徴とする熱硬化性ポリイミド樹脂アブリレグの製造方法。

【発明の詳細な説明】

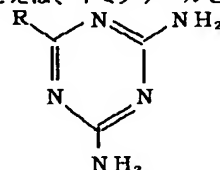
【0001】

【産業上の利用分野】本発明は、熱硬化性ポリイミド樹脂組成物及び熱硬化性ポリイミド樹脂アブリレグの製造方法に関するものである。

【0002】

【従来の技術】リジットプリント配線板とフレキシブルプリント配線板とを組合せ一体化したプリント配線板の接着には、ノーフローアブリレグといわれるアブリレグが使用されている。このノーフローアブリレグは、通常、多層プリント配線板を製造するとき、内層回路板相互間及び内層回路板と外層材とを接着するためのアブリレグと異なり、樹脂流れが極めて少ない(10%以下)アブリレグである。樹脂流れを少なくするのは、リジットプリント配線板とフレキシブルプリント配線板とを組合せ一体化するとき、アブリレグの樹脂がフレキシブルプリント配線板の領域にはみ出さないようにするためである。

【0003】このように樹脂流れが少ない接着用アブリレグの樹脂組成としては、熱硬化性ポリイミド樹脂、エポキシ樹脂及びジシアングリアミド(エポキシ樹脂の硬化剤として作用する)を基本的な成分とし、必要により硬化促進剤、たとえば、イミダゾールを配合したものが使



Rは、炭素数1～11のアルキル基又はフェニル基である。

【0006】熱硬化性ポリイミド樹脂及びエポキシ樹脂については、特に制限がなく、一般にプリント基板に用いられているものであればよい。2, 4-ジアミノ-s-トリアジンとしては、2, 4-ジアミノ-s-トリアジンとしては、アセトグアナミン、ビニルトリアジン、ベンゾグアナミン等が挙げられる。また、熱硬化性ポリイミド樹脂は、市販されている熱硬化型付加型マレイミド系ポリイミド樹脂例えばローヌアラン社のケイミ★50

*からなる熱硬化性ポリイミド樹脂組成物。

【化1】

10※用されている。一般に、アブリレグを製造するときの加熱時間を長くしたり、加熱温度を高くすると樹脂流れが少なくなる。しかしながら、熱硬化性ポリイミド樹脂、エポキシ樹脂及びジシアングリアミドを基本的な成分とする樹脂組成では、この方法によって樹脂流れが均一なアブリレグを得ることができない。そこで、接着用アブリレグの樹脂組成に変性樹脂を加えて、樹脂流れを調整するようにしている。変性樹脂としては、エポキシアクリレートやゴム弾性特性を有する樹脂が使用されている。

【0004】

20【発明が解決しようとする課題】ところが、変性樹脂を加えると、硬化後の樹脂のTgが低くなり、プリント配線板の耐熱性が悪くなる。また、熱膨張が大きくなるため、スルーホール信頼性を損なう。さらに、多層化後の薬品処理により、加えた変性樹脂が溶出したり膨潤するという欠点があった。本発明は、変性樹脂を添加しないでノーフローアブリレグを得ることができる樹脂組成物を得ようとするものである。

【0005】

30【課題を解決するための手段】本発明者らは、樹脂流れが少なく均一なアブリレグを得るための条件について種々検討を重ね、熱硬化性ポリイミド樹脂及びエポキシ樹脂の混合物を、化2で表される2, 4-ジアミノ-s-トリアジンで硬化させると、樹脂流れを均一に制御しやすいことを見出した。

【化2】

★ド601等が使用される。さらに、エポキシ樹脂は、2官能以上であれば特に制限がなく、ビスフェノールAジグリジルエーテル、フェノールノボラック樹脂のジグリシジルエーテルなどが使用される。これらの配合量は、熱硬化性ポリイミド樹脂10～80重量部、エポキシ樹脂20～90重量部、2, 4-ジアミノ-s-トリアジン1～20重量部である。特に2, 4-ジアミノ-s-トリアジンを3～10重量部配合したときに、樹脂

流れのコントロールが容易である。

【0007】本発明の熱硬化性ポリイミド樹脂組成物は、有機溶剤に溶解してワニスとし、これを繊維基材に含浸し、加熱して樹脂をBステージ迄硬化させてアリアレグとするが、このときの条件により樹脂流れを調整する。すなわち、樹脂の硬化を進めると樹脂流れが少なくなる。

【0008】アリアレグとしたときの樹脂流れのコントロールは、塗工温度における樹脂の反応性に依存する。アリアレグ樹脂配合の反応性は、示差走査熱量計 (Differential Scanning Calorimeter 以下DSCと記す) で測定できる。安定した樹脂流れを得るためには、DSCで測定した発熱開始温度が130~150℃、発熱ピーク温度が220~250℃になるようにするとよい。従来、多層化用アリアレグの硬化剤として多用されているジシアンジアミド等の脂肪族アミン脂肪族アミンは、塗工温度である130~160℃での反応が活発であり、DSCで測定した発熱開始温度が110℃、発熱ピーク温度が200℃である。

【0009】

【実施例】熱硬化性ポリイミド樹脂 (仏ローヌプーラン社製のケルイミド601) 25重量部、フェノールノボラック型エポキシ樹脂 (油化シェル株式会社製のエビコート154) 25重量部、アセトグアナミン5重量部を、ジメチルアセトアミド45重量部に溶解して、エポキシ変性ポリイミド樹脂配合ワニスを用意した。なお、この樹脂配合の反応性をDSCにより、昇温速度: 10℃/min (室温→300℃) で測定したところ、発熱開始温度は146℃、発熱ピーク温度は236℃であった。

【0010】厚み0.1mmのガラスクロスに固形樹脂分が、52重量%となるように前記エポキシ変性ポリイミド樹脂配合ワニスを含浸し、160℃で20分間加熱してアリアレグを得た。

【0011】比較例1

熱硬化性ポリイミド樹脂 (仏ローヌプーラン社製のケルイミド601) 25重量部、フェノールノボラック型エポキシ樹脂 (油化シェル株式会社製のエビコート154) 25重量部、ジシアンジアミド5重量部を、ジメチルアセトアミド45重量部に溶解して、エポキシ変性ポリイミド樹脂配合ワニスを用意した。なお、この樹脂組成の発熱開始温度は116℃、発熱ピーク温度は204℃であった。以下前記実施例と同様にしてアリアレグを得た。

【0012】比較例2

熱硬化性ポリイミド樹脂 (仏ローヌプーラン社製のケルイミド601) 25重量部、フェノールノボラック型エ

ポキシ樹脂 (油化シェル株式会社製のエビコート154) 25重量部、ジシアンジアミド5重量部、エポキシアクリレート20重量部を、ジメチルアセトアミド45重量部に溶解して、エポキシ変性ポリイミド樹脂配合ワニスを用意した。なお、この樹脂組成の発熱開始温度は116℃、発熱ピーク温度は204℃であった。

【0013】以上得られたアリアレグについて、樹脂流れを調べた。また、170℃で90分間加熱して樹脂を硬化させ、Tgを調べた。次に、回路を形成したリジッドプリント配線板とフレキシブルプリント配線板との間に得られたアリアレグを挟み、温度170℃、圧力2.5MPaで加熱加圧してリジッドプリント配線板とフレキシブルプリント配線板とを一体化した。そして、ボイド発生の有無、及び、スルーホール信頼性を調べた。その結果は、表1の通りであった。

【0014】樹脂流れの測定法は次の通りである (IPC-TM-65準拠)。アリアレグの端から25mm以上内側に入ったところから、101.6mm角の試料を4枚バイアスカットし重量 (初期重量) を測定する。試料は、アリアレグのロールから所定の間隔で採取し数セット用意する。4枚の試料を方向を揃えて重ね、ポリフッ化ビニルのフィルムを介して銅板ではさみ、171℃、1.37MPaで10分間加熱加圧する。冷却後試料の中央から直径81.1mmの円盤に打ち抜き、打ち抜かれた円盤の重量を測定し、次の式 (数1) で樹脂流れを計算する。

【数1】樹脂流れ (%) = $100 \times (\text{初期重量} - 2 \times \text{円盤重量}) / \text{初期重量}$

【0015】ボイドの有無は次のようにして調べた。基材厚さ0.1mmの両面銅張積層板 (銅はく厚さ35μm) の表裏全面に直径1.6mmのクリアランスホールを設け、残銅率を50%とした回路パターンを作成する。その両面にテストするアリアレグを介して厚さ18μmの銅はくを重ね、170℃、2.5MPaで90分間加熱加圧する。そして、外層の銅はくをエッチング除去し、クリアランスホールへの埋め込みを調べる。

【0016】スルーホール信頼性は次のようにして調べた。テストするアリアレグを10枚重ね、その外側に厚さ18μmの銅はくを重ね、170℃、2.5MPaで90分間加熱加圧する。直径0.4mmのスルーホールを設け、穴内のめっき厚さが35μmになるようにスルーホールめっきをする。その後スルーホール100穴間で表裏回路を交互に導通するような回路パターンに加工する。そして、20±2℃の流水槽に10秒浸漬、260±2℃のホットオイル槽に10秒浸漬を1サイクルとするホットオイル試験100サイクル実施する。

【0017】

【表1】

	実施例	比較例1	比較例2
樹脂流れ (%)	3.5	10.7	8.6
樹脂流れのばらつき (%)	2.1~5.5	0.1~15.2	2.0~9.0
Tg (°C)	176	167	57
ボイドの有無	○	△~×	○
スルーホール信頼性	異常無し	断線	断線

ボイドの有無：○；異常無し、△；小さなボイドあり、×；ボイド多発又は断線

【0018】表1から、実施例の樹脂組成物は、アリア
レグとしてとき、樹脂流れのコントロールが容易であ
り、同一条件で塗工している間中の樹脂流ればらつきが
少ない上に、硬化後のTgが高いことがわかる。また、
接着後のボイドの発生も認められず、スルーホール信
頼性も良好である。

* 【0019】

【発明の効果】本発明によれば、エポキシ変性ポリイミ
ド樹脂組成物の硬化剤として、2，4-ジアミノ-s-
トリアジンを使用することにより、変性樹脂を配合しな
いでもアリアレグの樹脂流れを少なくかつ均一にでき
る。

フロントページの続き

(51)Int. Cl. ⁶	識別記号	片内整理番号	FI	技術表示箇所
C08L 79/08	LRB		C08L 79/08	LRB
C09J 179/08	JGE		C09J 179/08	JGE

(72)発明者 酒井 広志

茨城県下館市大字小川1500番地 日立化成
工業株式会社下館工場内